Diffusion-controlled subcritical crack growth in the presence of a dilute gas environment

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Summary

A simple two-step, diffusion-reaction concept of subcritical crack growth is proposed for brittle fracture in the presence of a reactive gas environment. A detailed model for the diffusion step is developed from the kinetic theory of gases, on the assumption that collisions between diffusing gas molecules and crack walls determine the flow rate. The temperature and stress conditions under which diffusion is expected to be the controlling factor are then discussed, with particular reference to the system $SiO_2-H_2O(g)$. Hertzian fracture tests on glass in vacuum and dilute water vapour environments, and over a range of temperatures, provide supporting evidence for the model.

1. INTRODUCTION

With many highly brittle solids the presence of a suitable reactive environment causes cracks to grow at subcritical stress levels. The basic mechanism is envisaged as a stress-enhanced chemical interaction between the environmental species and the crack-tip bonds, the crack growing at a rate determined by the reaction kinetics. There may, however, exist a whole sequence of subsidiary rate-dependent steps leading up to the reaction stage; these demand consideration, for the slowest step in the chain of events must ultimately control the rate of crack advance. In particular, the fine scale of the wall separation in typical brittle crack configurations suggests that transport processes may play a significant role in limiting the rate of supply of reactive material to the crack tip region.

An important model crack system which has recently received considerable attention, particularly from Wiederhorn and co-workers[1-3], is that of silicate glass in the presence of water in either its liquid or vapour phase. In liquid form environmental water maintains close contact with the growing crack by means of a rapid capillary action; only when the crack approaches its terminal velocity does fluid viscosity appear to appreciably retard the transport process. Consequently, subcritical crack growth in the system $SiO_2-H_2O(\ell)$ is governed almost entirely by reaction kinetics[2]. In vapour form, however, the transport of moisture along the crack is inhibited by interfacial diffusion processes, particularly under "dilute gas" conditions in which the mean free path between intermolecular collisions greatly exceeds the typical crack-wall separation. This impedance in molecular flow rate to the tip noticeably limits the subcritical crack velocities in the system $SiO_2-H_2O(g)$[3].

In the present paper the attention centres on the role of molecular diffusion processes in the control of subcritical crack growth in a gaseous environment. A model for molecular flow along the fracture interface is first derived from basic kinetic theory of gases. Results from Hertzian fracture tests on the $SiO_2-H_2O(g)$ system are then used to provide qualitative support for the model.

2. KINETICS OF CRACK GROWTH

We consider the fracture mechanics of a crack of length c, unit width along OZ, in the presence of a reactive gas environment (Fig. 1). For a virtual extension dc the number of
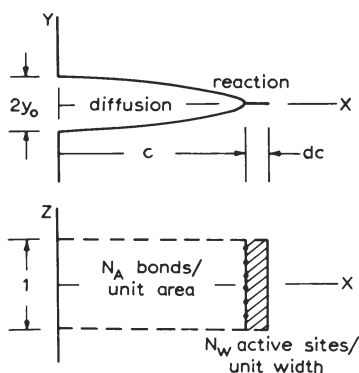
Fig. 1. Two-step model of subcritical crack growth. Environmental species diffuses along interface and reacts with crack-tip bonds.

crack-tip bonds that need to be ruptured is

$$dN = N_A \, dc$$

where N_A is the number of bonds intersecting unit area of crack plane. If bond rupture proceeds according to a time-dependent mechanism the crack front will advance with a velocity

$$v_c = \frac{dc}{dt} = \frac{1}{N_A} \frac{dN}{dt}. \qquad (1)$$

The crack velocity therefore provides a direct measure of the kinetics of the rate-controlling process.

A gas molecule entering the crack mouth may undergo several kinetic events before reacting with bonds at the crack tip. However, for the experimental conditions to be considered later it will suffice to treat the kinetics of crack growth in terms of a simple two-stage, diffusion-reaction process[4]. The reaction is generally taken to be thermally activated, with η molecules of gas combining with a crack-tip bond to form an activated complex and thereby leading to rupture:

$$\eta G + B \rightarrow B^*. \qquad (2)$$

η is then the order of the reaction. As the crack advances the chemisorbed products are left behind on the newly created surfaces. The rate of bond rupture, dN/dt, is related to the steady-state molecular flow rate, dM/dt, along the crack interface by

$$\frac{dN}{dt} = \frac{1}{\eta} \frac{dM}{dt}. \qquad (3)$$

The diffusion and reaction processes both act to regulate the pressure differential $(p_o\text{-}p_c)$ between the crack mouth (source) and tip (sink); if the diffusion is slower the supply of molecules at the crack tip is quickly depleted $(p_c \ll p_o)$, whereas if the reaction is slower the crack-tip pressure builds up to nearly that of the surrounding environment $(p_c \rightarrow p_o)$.

3 DIFFUSION OF A DILUTE GAS

We look first at the diffusion step in the two-stage process (Fig. 2). If the crack-mouth opening greatly exceeds the mean free path of the gas molecules the initial flow into the crack will be characteristic of a continuous, low-viscosity fluid. But as the crack tip is approached there must be a point, at $x = x_1$ say, beyond which molecules will collide more frequently with the crack walls than with their neighbours. This situation will persist until the gas molecules finally impinge on the crack-tip bonds at $x = x_2$. The so-called "free molecular flow" between x_1 and x_2 is then determined by the nature of the molecular scattering at the crack walls. An extensive study of gaseous flow through narrow channels by Knudsen[5] shows that the scattering is highly diffuse, and that the flow rate consequently becomes attenuated. Thus in the crack problem free molecular flow may control interfacial diffusion over a significant portion, if not all, of the crack length. For example, the mean free path for air molecules at s.t.p. is 0.1 μm, which corresponds to the crack-wall separation at a distance $x_2 - x_1 \simeq 1$ mm from the crack-tip bonds in a typical brittle solid.

The molecular flow rate may be deduced from the kinetic theory of gases. An elemen-
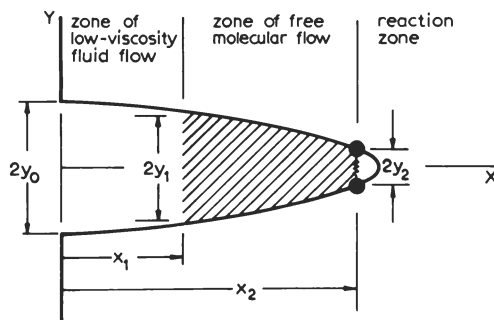

Fig. 2. Flow and reaction zones along crack interface.

tary treatment[6] gives the number of molecules in the environment crossing unit area in unit time as

$$\frac{1}{4} n_0 \bar{v}$$

where the molecular density n_0 and the mean molecular velocity $\bar{v}$ are given by

$$n_0 = \frac{p_0}{kT}, \quad \bar{v} = \left(\frac{8kT}{\pi m}\right)^{1/2} ;$$

k is the Boltzmann constant, T the absolute temperature, and m the molecular mass. An upper bound to the flow rate occurs in the idealised situation in which the gas is "dense" $(x_1 \to x_2)$ and of negligible viscosity, and the reaction is "instantaneous"$(p_c \to 0)$; the environment then has direct access to the cross-section A_2 at the crack-tip bonds, giving

$$\frac{dM}{dt} = \frac{1}{4} n_0 \bar{v} A_2 = \frac{p_0 A_2}{(2\pi mkT)^{1/2}} .$$

For more general flow conditions this equation requires only simple modification. Thus, as the gaseous environment is made more dilute and a zone of free molecular flow develops behind the crack tip, an "impedance factor" K may be introduced to account for the resulting attenuation[7]. Again, the effect of a finite reaction rate may be treated in terms of a reverse flow arising from pressure build-up at the crack tip. The net flow rate therefore becomes

$$\frac{dM}{dt} = \frac{(p_0 - p_c)KA_2}{(2\pi mkT)^{1/2}}. \tag{4}$$

An expression for the crack velocity may now be obtained by combining eqns. (1), (3) and (4);

$$v_c = v_d (1 - p_c/p_0) \tag{5}$$

where, at $p_c \ll p_0$,

$$v_d = \frac{p_0 KA_2}{\eta N_A (2\pi mkT)^{1/2}} \tag{6}$$

represents a diffusion-controlled upper limit to the subcritical growth rate.

The geometry-dependent impedance factor K is computed from collision dynamics, on the assumption that the scattering of molecules at the channel walls is perfectly diffuse. Its value is necessarily unity for an infinitesimally short channel, and decreases as the channel becomes longer and narrower. For the particular case of a long channel of varying cross-section area A, perimeter P, Knudsen[5] gives the expression

$$K = \left\{ \frac{3A_2}{16} \int_{x_1}^{x_2} \frac{P}{A^2} \, dx \right\}^{-1} .$$

In terms of a crack of rectangular cross section (Fig. 1) with $c \gg 1 \gg 2y_0$ we have $A = 2y$, $P = 2 + 4y \simeq 2$. This gives

$$K = \left\{ \frac{3A_2}{32} \int_{x_1}^{x_2} \frac{dx}{y^2} \right\}^{-1} . \tag{7}$$

In evaluating the integral in eqn. (7) Bradshaw[8] makes use of the continuum elasticity result that near to the crack tip, where the attenuation in flow will be most pronounced, the crack profile should be very nearly parabolic. Expressed in the notation of fracture mechanics we have, to good approximation[9],

$$y = \frac{2\mathcal{K}}{E} \left[\frac{2}{\pi} (c - x) \right]^{1/2} \tag{8}$$

where E is Young's modulus and $\mathcal{K}$ is the stress-intensity factor. The parameter $\mathcal{K}$ relates the intensity of the elastic field in the near vicinity of the crack tip to external loading conditions. Upon substituting eqn. (8) into eqn. (7) and integrating, we have

$$KA_2 = \frac{64(\mathcal{K}/E)^2}{3\pi \ln(y_1/y_2)} . \tag{9}$$

It is of interest to express the crack-velocity equations in a reduced form for the specific system glass—water, retaining p_0, T, and $\mathcal{K}$ as independent variables. We assume one molecule of water vapour to react with one Si—O bond at the crack tip, i.e. $\eta = 1$, and take $N_A = 3.5 \times 10^{18}$ bonds m^{-2} (glass), $m = 3.0 \times 10^{-26}$ kg (H_2O), $E = 7.0 \times 10^{10}$ Nm^{-2} (glass). The crack-wall displacements at the limit of the free-molecular-flow zone are more difficult to specify, but any uncertainties here will have only a minor influence on the slowly-varying logarithmic term in eqn.

(9). The displacement y_1 will be determined by either the mean free path of the surrounding gas, or by the crack-mouth opening, whichever is the smaller; y_2 may be interpreted as an effective cut-off displacement where the crack-tip bonds are exposed to the arriving gas molecules. Putting, say, $y_1 = 1$ μm, $y_2 = 0.5$ nm, eqns. (6) and (9) combine to give

$$v_d = 3.23 \times 10^{-17} p_0 T^{-1/2} \mathcal{X}^2 , \qquad (10)$$

with all parameters in S.I. units. A distinguishing feature of the diffusion-limited velocity eqn. (10) [compare the reaction-controlled velocity eqn. (15), later] is the relative insensitivity to variations in temperature and external loading.

To illustrate the magnitude of the effect, we consider the special case of a crack in glass loaded just below its critical level[2], taking $\mathcal{X} = 7 \times 10^5$ Nm$^{-3/2}$, in the presence of saturated water vapour at room temperature, i.e. $p_0 = 3.0 \times 10^3$ Nm^{-2} (24 Torr), $T = 300$ K. From eqns. (6) and (9), with $A_2 = N_A^{-1/2} = 5.4 \times 10^{-10}$ m^2, we calculate $v_d = 2.7 \times 10^{-2}$ Kms^{-1}, $K = 9.0 \times 10^{-2}$, i.e. $v_d = 2.4 \times 10^{-3}$ ms^{-1}. This is of the same order of magnitude as the limiting subcritical velocities observed by other workers[3,10] for glass in saturated atmospheres.

4. INCORPORATION OF REACTION KINETICS

The kinetics of the reaction step in the glass—water system has been well documented by Wiederhorn and co-workers[1-3], and only the essential details will be presented here. For the thermally activated chemical reaction of eqn. (2) the rate of bond rupture may be written

$$\frac{dN}{dt} = N_w \kappa \qquad (11)$$

with N_w the number of active bond sites per unit width of crack front (Fig. 1), and κ the reaction rate constant for one bond. From the theory of absolute reaction rates[11]

$$\kappa = \frac{kT}{h} \left\{ \exp\left(-\frac{\Delta F_r^*}{kT}\right) - \exp\left(-\frac{\Delta F_p^*}{kT}\right) \right\} ,$$

where h is Planck's constant, and ΔF_r^*, ΔF_p^* are the free energies of formation of the activated complex from reactant and products respectively. One seeks a free energy function of the form $\Delta F^*(p_c, T, \mathcal{X})$, and considers the non-equilibrium state $\Delta F_r^* < \Delta F_p^*$ so that the reverse reaction (desorption) associated with the second exponential term may be ignored. Proceeding along these lines Wiederhorn[1] reduces the reaction rate to

$$\kappa = C(T) p_c^\eta \exp\left(\frac{-E^* + b\mathcal{X}}{kT}\right) , \qquad (12)$$

where $C(T)$ is a slowly-varying temperature-dependent term, E^* is an activation energy, and $b\mathcal{X}$ is a term arising from free energy reduction as the external loading is applied. The linear dependence of free energy on $\mathcal{X}$ is introduced into the treatment in a somewhat arbitrary manner, but appears to be borne out by experimental observation.

From eqns. (1), (11) and (12) the crack velocity may be written in the form

$$v_c = v_r (p_c / p_0)^\eta \qquad (13)$$

where, at $p_c \to p_0$,

$$v_r = \frac{N_w}{N_A} C(T) p_o^\eta \exp\left(\frac{-E^* + b\mathcal{X}}{kT}\right) \qquad (14)$$

represents the subcritical growth rate under reaction-controlled conditions. Equation (14) may be regarded as a semi-empirical relationship with three adjustable parameters. A good fit to Wiederhorn's crack-velocity data for soda-lime glass in water vapour is given by

$$v_r = 0.46 \, p_o^\eta \exp\left(\frac{-1.31 \times 10^4 + 1.32 \times 10^{-2} \mathcal{X}}{T}\right)$$

$$(15)$$

with all quantities again in S.I. units. The high sensitivity of this expression to temperature and external loading is noted.

The unknown quantity p_c may now be eliminated from eqns. (5) and (13) to give the following implicit equation in crack velocity for the composite diffusion-reaction process:

$$\frac{v_c}{v_d} + \left(\frac{v_c}{v_r}\right)^{1/\eta} = 1 . \qquad (16)$$

For the special case of a first-order reaction as

considered earlier the crack velocity reduces simply to the harmonic mean of limiting values,

$$\frac{1}{v_c} = \frac{1}{v_d} + \frac{1}{v_r} . \qquad (17)$$

Referring to eqns. (10) and (15) for v_d, v_r we then see that subcritical growth is either diffusion- or reaction-controlled according to whether T and $\mathcal{X}$ are large or small. This is illustrated in Fig. 3, in which eqn. (17) is plotted for soda-lime glass in a water-vapour environment at $p_o = 3 \times 10^2$ Nm^{-2} (2 Torr); as the level of stress intensity and temperature increases the curve shows an initial rapid rise followed by an abrupt "saturation" as first eqn. (15) then eqn. (10) controls the kinetics.

5. HERTZIAN FRACTURE TESTS

It is evident from Fig. 3 that the relative importance of the diffusion and reaction steps in subcritical crack growth must ultimately depend on the stress and thermal conditions operative in a given fracture test. In particular, at high levels of stress or temperature it is interfacial diffusion of the vapour phase that is expected to be the determining factor in the kinetics of fracture.

Evidence favouring the proposed diffusion model has been obtained from Hertzian fracture tests[12] made in these laboratories on
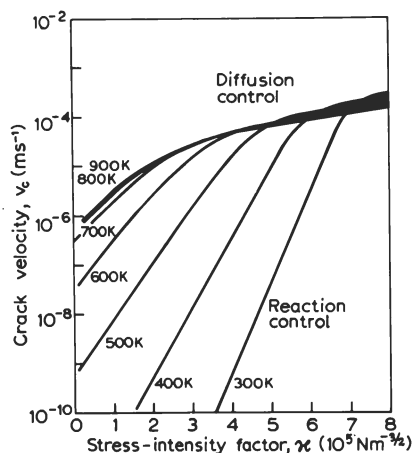

Fig. 3. Subcritical crack velocities for soda-lime glass in water vapour at pressure 3×10^2 Nm^{-2}. Note high sensitivity of crack velocity to stress intensity, temperature, in reaction-controlled region (lower, straight-line portions), low sensitivity in diffusion-controlled region (upper, saturated portions). Crack becomes critical at $\mathcal{X} = 7 - 8 \times 10^5$ Nm$^{-3/2}$.

soda-lime glass slabs. In the Hertzian test a spherical indenter is loaded on the specimen surface at a constant rate until, at a critical load P_c, a cone-shaped fracture suddenly grows downward from just outside the circle of contact. Initially, the crack develops from a surface flaw into a shallow ring which propagates to a critical depth prior to flaring into the cone[13]. Under environment-free conditions this surface ring is stable, its depth increasing only as the indenter load is applied; under the influence of a reactive atmosphere, however, the growth of the ring is enhanced by the action of kinetic processes. Thus the main effect of the environment is to cause premature extension to a critical depth, the resulting reduction in P_c reflecting the magnitude of the subcritical crack velocity.

The Hertzian tests were carried out in an environmental chamber designed with special facility to vary gas pressure, specimen temperature and indentation site through external control units[14]. Some 200 cone cracks were formed on a single abraded glass surface 50 mm square, over a temperature range 0—500°C and at a fixed load rate 40 Ns^{-1}. The tests were made in two runs, one in vacuum ($p_o < 10^{-4}$ Nm^{-2}) and the other in a dilute water-vapour environment ($p_o = 3 \times 10^2$, Nm^{-2}). Figure 4 shows the results. The adverse effect of the reactive environment on critical load is apparent.

A detailed interpretation of such data in terms of subcritical phenomena requires a fracture-mechanics analysis of the development of the surface ring up to the point of instability. In general, the complexity of the Hertzian contact problem precludes an analytical solution, and one must resort to computer techniques[15]. However, with the simple trend in Fig. 4, the near-parallel water-vapour and vacuum curves implying a temperature-insensitive subcritical crack velocity, the case for diffusion control of the Hertzian fracture kinetics may be argued on a purely qualitative basis. We need only appreciate that while the *load* rate is maintained constant in our tests, the *stress intensity* rate diminishes rapidly with time. The time average of $\mathcal{X}(t)$ is therefore likely to be heavily weighted toward the critical value at cone formation. Under such conditions the right-hand side of Fig. 3 will govern the crack-velocity response; that is, all environment-formed cone cracks will have
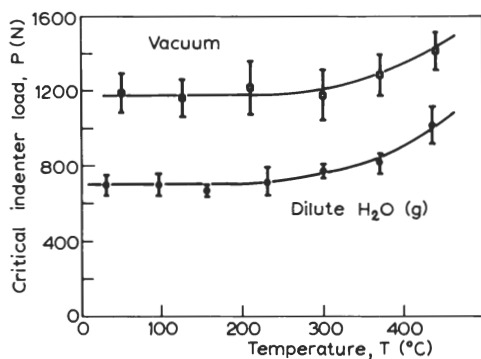
Fig. 4. Hertzian fracture tests on soda-lime glass. Indenter diam. 12.7 mm, load rate 40 Ns^{-1}. Glass surface preabraded with No. 500 SiC powder to give maximum reproducibility in results. Tests in vacuum and dilute water vapour (pressure as in Fig. 3). Each data point represents mean of at least 10 tests. Error bars denote one standard deviation. (Data courtesy of M.V. Swain.)

similar, diffusion-controlled growth histories, regardless of temperature.

6. DISCUSSION

The two-step model for the rate control of subcritical crack growth appears to be in accord with the observed behaviour of the $SiO_2 - H_2O(g)$ system. By virtue of its favourable loading routine the Hertzian test operates predominantly at high stress intensities, and thereby reflects the characteristics of the diffusion-controlled step. It should be pointed out, however, that other fracture tests may well tend to low stress-intensity, reaction-controlled conditions, in which case a rapid divergence between water vapour and vacuum results with increasing temperature would be anticipated.

In deriving the transport equations in Sect. 3 it was necessary to make several implicit assumptions and approximations:

(i) The possibility that simultaneous diffusion mechanisms (e.g. surface diffusion along the crack walls) may compete with free molecular flow was ignored. In view of the tendency for diffusion in other than the gaseous phase to be thermally activated one may justify this oversight on the basis of the temperature insensitivity of the Hertzian fracture data.

(ii) The chemisorption reaction (2) is postulated as the only sink for diffusing gas molecules along the fracture interface. If water vapour were to condense on the newly created glass fracture surfaces, or preferentially at the crack tip, this assumption would clearly be violated. However, under the experimental conditions considered here, namely elevated temperatures and below-saturation gas pressures, the lifetime of molecules in the physisorbed state is likely to be negligibly small.

(iii) In the diffusion-limited, crack-velocity equation (6), the geometrical factor KA_2 is the main source of uncertainty. Strictly, the calculated expression (9) holds only for a long, parabolic free-molecular-flow zone with well-defined entrance and exit points. The Hertzian surface-ring cracks considered in Sect. 5 are certainly long in comparison with the crack-wall separation, but not with the ring circumference. Again, the approximation of a parabolic crack contour is reasonable only over distances from the crack tip small compared with the crack length. The vague interpretation of the limiting crack-wall displacements y_1, y_2 (Fig. 2) adds further complication. The gas flow does not change its character from viscous to molecular across a distinct boundary, but passes rather through a gradual "transition" stage embracing an approximate range 100 M.F.P. $> 2y_1 >$ M.F.P. in crack-wall separation[6] (M.F.P. = mean free path); the flow into the reaction zone passes through a similarly indistinct region in which van der Waals interaction between the narrowing crack walls and diffusing molecules significantly modifies the collision dynamics*. Fortunately, none of the above shortcomings manifests itself as a rapidly-varying element in the theory, and the calculation would appear to be within the bounds of order-of-magnitude accuracy.

(iv) The treatment assumes a quasi-steady state in the gaseous flow, disregarding the motion of source and sink as the crack propagates. This simplification is valid only if the velocity of the diffusing molecules along the

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* This will be of special importance for configurations in which the gas molecule, by virtue of either its own large size or the narrowness of a highly brittle crack, is constrained to make prolonged contact with the interface walls on approaching the tip. Such size considerations (cf. O—H bond length 0.097nm in the water molecule with Si—O bond length 0.162 nm in the glass network) suggest that the effect should not be prominent in the system studied here.

interface, v_m, greatly exceeds the velocity of the crack tip, v_c. Now, in the notation of Sect. 3, we have the straightforward relation

$$\frac{dM}{dt} = nAv_m \ ;$$

in steady flow, dM/dt remains constant along the free-molecular-flow zone. Combining this relation with eqns. (1) and (3) gives

$$\eta N_A v_c = nAv_m \ .$$

With $A = 2y$, $n = p/kT$, the requirement $v_m \gg v_c$ becomes

$$p \ll \frac{\eta N_A kT}{2y} \ .$$

Choosing unfavourable conditions, we insert $N_A = 3.5 \times 10^{18}$ bonds m^{-2} (glass), $T = 300K$, $\eta = 1$, $2y_o = 1$ μm (typical upper limit to crack-mouth opening in a Hertzian cone crack), reducing the above condition to

$$p_o \ll 1.5 \times 10^4 \ Nm^{-2} \ .$$

Thus the diffusion problem may be regarded as quasi-static only for very dilute gas environments.

Finally, the dominance of molecule—wall collisions within the free-molecular-flow zone implies that different components of a gaseous mixture will diffuse to the crack tip independently of each other. Hence the introduction of a second *reactive* species would act to enhance the diffusion-limited crack velocity according to the following simple modification of eqn. (6):

$$v_d = \frac{KA_2}{N_A (2\pi kT)^{1/2}} \left(\frac{p_{c1}}{\eta_1 \sqrt{m_1}} + \frac{p_{o2}}{\eta_2 \sqrt{m_2}} \right) \ .$$

The component with large partial pressure, small molecular mass, will therefore tend to control. If, on the other hand, the second species were to be *non-reactive*, the effect would be less simple to predict. If the added component serves merely to increase the total pressure of the environment a slightly enhanced growth may result from an attendant reduction in the length of the molecular flow zone; if, however, the non-reactive species physisorbs strongly at the tip region (where the van der Waals interactions with the surrounding walls are likely to be most intense) the crack front may become "poisoned", and further advance thereby inhibited[16].

The gaseous flow model presented in this paper has been developed from first principles, with no adjustable parameters, and involves only basic parameters of the brittle crack system and its environment. The extension of the model to less brittle materials, such as metals and alloys[17,18] where crack-tip plasticity plays a major role in the geometry and mechanics of fracture, would appear to demand an added degree of sophistication in the treatment.

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